radii of these ions follow the same order as that given by Bragg[25] and by Wasastjerna[26] for the radii of ions in crystals; moreover, the difference is roughly constant, the effective radii of the ions in solution being about 0.47 Å. greater than those of Bragg for radii in crystals.

The author expresses his thanks to Professor P. Debye of this Institute, whose advice in connection with this problem has been constantly sought and freely given.

Summary

The free energy of hydration of a chemically unhydrated ion is obtained as a function of its radius by calculating the difference in energy necessary to charge the ion in a vacuum and that necessary to charge the ion in water and to compress the solvent in the vicinity of the ion. Regard is taken of the fact that the dielectric constant of a molecular medium is not constant in the vicinity of an ion.

The partial molal volume of an ion at great dilution is calculated as a function of its effective radius in solution. This calculation requires a further one for the contraction of the solvent (electrostriction) due to the pressures resulting from the attraction of the solvent dipoles by the ion.

The solution of the two resulting equations, obtainable for an electrolyte whose free energy of hydration and partial molal volume are known, gives the radii of the individual ions, and hence their free energies of hydration. The free energies of hydration of the most common ions are obtained in this way, and the consequent calculations of electron affinities and lattice energies are made.

ZÜRICH, SWITZERLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, GEORGE WASHINGTON UNIVERSITY AND THE FIXED NITROGEN RESEARCH LABORATORY]

THE PHOTO- AND RADIOCHEMICAL INTERACTION OF HYDROGEN AND CHLORINE

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The development and present status of the theory of the photosynthesis of hydrogen chloride have been so recently and thoroughly summarized[2] that no further review is required. The synthesis by other radiative agencies such as α-, β-, γ- and x-rays was discussed and some of the possible relations to photochemical mechanism were earlier pointed out by Lind.[3]

[25] Bragg, *Proc. Roy. Inst. Gr. Brit.*, [III] **24**, no. 119, 614 (1925).

[26] Wasastjerna, *Soc. Scient. Fenn. Comm. Math.-Phys.*, **1**, p. 38 (1923).

[1] Frank Porter, *Thesis*, George Washington University, **1926**.

[2] A. L. Marshall, *Trans. Am. Electrochem. Soc.*, Reprint 9, April, **1926**. A. J. Allmand, *Ann. Repts. Chem. Soc.*, **22**, 333 (1925).

[3] Lind, "Chemical Effects of α-Particles and Electrons," Chemical Catalog Co., New York, **1921**.

It will suffice to review these connecting links briefly as constituting the starting point of the present work.

Bodenstein[4] made the first serious attempt to correlate the photo- and radiochemical reaction mechanisms. He was struck by the excessive value[5] (100–1000) for the number of molecules of hydrogen chloride synthesized for each ion pair produced in the stoichiometric mixture by alpha radiation. This suggested to him a free-electron chain mechanism which he proposed as a general photochemical theory, and which seemed particularly applicable to those photochemical reactions which greatly exceed the predictions of the Einstein photochemical equivalence law. Later, Bodenstein[6] abandoned this "wandering electron" theory of photo-action in favor of a chain mechanism propagated by freshly formed molecules of the product, hydrogen chloride, which retain the energy of reaction for a short time and can transfer by collision sufficient of it to activate other chlorine molecules. This "hot-molecule" theory and the Nernst[7] atomic-chain theory are the two principal contenders at the present time in the explanation of the chain mechanism.

Before the electron-chain theory was abandoned, however, Bodenstein[6] and Taylor[8] measured the synthesis of hydrogen chloride under alpha radiation from radon, using the thin α-ray bulb of Lind[9] and determining the reaction rate by chemical methods. A value of $+M_{\mathrm{HCl}}/N_{(\mathrm{H_2}+\mathrm{Cl_2})} = 4000$ was found which, while higher than that from the β-ray results of Jorissen and Ringer[10] was very far below Bodenstein's value of $+M_{\mathrm{HCl}}/q = 10^6$ for the photo reaction.[11] Although Taylor realized that the photosensitivity of his gas mixture was less than that of Bodenstein and Dux, he apparently assumed that the difference of 250-fold had some basis of reality, since he stated that "the comparability of the two reactions in this regard is, therefore, in good measure established."

This raised an interesting question as to the nature of the comparison factor of 250. Although Bodenstein's free-electron theory of the photo reaction of hydrogen and chlorine had to be abandoned on account of the absence of ionization, Lind[12] suggested that since there is no lack of ionization in the α-ray reaction, the theory might still be applicable there, unless Bodenstein's supposition that the mechanism is identical in both cases is correct.

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[4] Bodenstein, *Z. physik. Chem.*, **85**, 389 (1913).

[5] Lind, *J. Phys. Chem.*, **16**, 610 (1912).

[6] Bodenstein, *Z. Elektrochem.*, **22**, 53 (1916).

[7] Nernst, *ibid.*, **24**, 335 (1918).

[8] Taylor, THIS JOURNAL, **37**, 24 (1915); **38**, 280 (1916).

[9] Lind, *Am. Chem. J.*, **47**, 397 (1912).

[10] Jorissen and Ringer, *Ber.*, **39**, 2095 (1906).

[11] M_{HCl} is the number of hydrogen chloride molecules formed; $N_{(\mathrm{H_2}+\mathrm{Cl_2})}$ is the number of ions produced in hydrogen and chlorine; q is the number of quanta of light energy absorbed.

[12] Ref. 3, p. 140.

Since 1921, however, it has become increasingly difficult to assume a chain reaction propagated by free electrons. As the cases of quantitatively studied α-ray reactions have been multiplied, further indications of chain reaction have been conspicuously absent. To explain the apparent exception of the hydrogen-chlorine reaction the assumption was still possible that the ion reaction was normal with a low M/N value, but that superimposed upon it was a small fraction of *atomization* of chlorine which by the Nernst mechanism and the high M/q value of Bodenstein would account for the moderately high M/N value found. Owing to the very long atom chain (10^6), the atomization required would be less than 0.5% of the ionization in order to account for Taylor's $M_{HCl}/N = 4000$. However, since this supposed difference between M/N and M/q is shown by the present work not to exist, or rather to have a low value in the opposite direction from unity, a new hypothesis must be based on entirely different considerations (see Discussion).

In order, however, to make a valid comparison of the reactivity of a hydrogen-chlorine mixture toward light and toward α-rays, it is necessary to employ a mixture of the same sensitivity or preferably the same mixture in both cases. We therefore planned to expose the same mixture at various sensitivities to light and to alpha radiation either separately or simultaneously. For this purpose we have returned to the use of the Bunsen and Roscoe actinometer so modified as to enable us to compare at various sensitivities the reactivity toward light and toward α-rays, as well as to study the temperature coefficient of the reaction under identical conditions.

Modified Bunsen and Roscoe Actinometer.—The original apparatus of Bunsen and Roscoe[13] for measuring the velocity of combination of hydrogen and chlorine consisted of a glass radiation chamber containing water to absorb the freshly formed hydrogen chloride. The diminution in gas volume thus produced was measured at constant pressure by the rate of motion of a water index column along a graduated capillary tube as it is drawn in under atmospheric pressure to restore the volume diminished by the absorption of hydrogen chloride in the reaction chamber to which the capillary is attached. The small volume of the capillary provides great sensibility of measurement, provided the temperature of the system be kept constant.

In order to use this system for alpha radiation also, it is only necessary to mount a thin α-ray bulb in the reaction chamber as was done by Bodenstein and Taylor. In our experiments, however, with water present as absorbent, the α-ray bulb cannot be mounted in the same chamber, because the bombardment by α- and β-rays would generate oxygen[14] which is well known to inhibit[15] the reaction strongly. It was also found inad-

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[13] Bunsen and Roscoe, *Pogg. Ann.*, **100,** 43 (1857).

[14] Duane and Scheuer, *Le Radium*, **10,** 33 (1913).

[15] Chapman and MacMahon, *J. Chem. Soc.*, **95,** 959 (1909).

visable to have the α-ray bulb in the light chamber on account of the difficulty of shutting off the alpha radiation at will.[16]

The final system adopted is shown in Fig. 1, where it will be seen that separate chambers are provided for photoradiation, alpha radiation and water absorption. This is quite allowable because the total volume of the actinometer does not affect the differential volume being directly measured.

To provide rapid mixing of the gases and opportunity for absorption, an all-glass electromagnetic circulating pump was devised which is described elsewhere.[17]

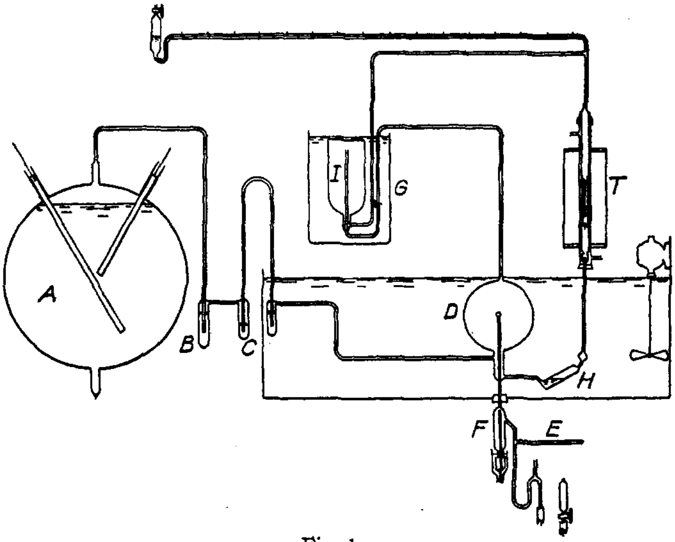

Fig. 1.

Such a system gives great flexibility of use and has proved very advantageous in simultaneously comparing reactions in the same mixture, either at different temperatures or under different forms of radiation. It is evidently capable of wide variations in employment, the possibilities of which are by no means exhausted in the present work.

Details of Apparatus.—A (Fig. 1) represents the generator in which a mixture of hydrogen and chlorine is electrolyzed from concd. hydrochloric acid. The electrodes are rods of dense graphite which make a fairly snug fit in the glass sleeves sealed to and projecting outward from the glass balloon. Complete seal is obtained by a layer of fused silver chloride (next to the acid) backed by a layer of lead, then a layer of wax and finally a mercury seal.

The gases from A pass through a bubbler B containing water to remove vapors of hydrogen chloride, then through the double trap C containing dil. sulfuric acid. This trap serves to isolate the generator from the rest of the system. The surface tension

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[16] Even if gaseous radon be withdrawn, RaC persists for four hours giving alpha radiation in diminishing amount.

[17] Porter, Bardwell and Lind, *Ind. Eng. Chem.*, 18, 1086 (1926).

of the solution lodging in a small constriction in the capillary tube uniting the two sides of the trap offers sufficient resistance to prevent movement of water through the trap during measurements.

The reaction sphere D contains at its center the source of alpha radiation in the form of radon confined in a thin α-ray bulb, 1.5 mm. in diameter and having a wall 5.7 microns thick, equivalent in stopping power toward α-rays to about 1 cm. of air. The details of making,[18] mounting and using[19] these bulbs have been previously described. A new method of determining the wall thickness by interference bands has been found superior to previous methods.[20]

Radon was introduced by breaking a thin tube of it by means of a magnetic hammer inside the side arm E. Before breaking it a liquid air-charcoal vacuum was produced in the system, so that the purified radon could be confined by mercury just at the shoulder of the small α-ray bulb. Before putting the mercury into place, the radon was condensed just below the reaction sphere by a liquid-air mop. The mercury was then brought just below the radon before it was released by warming, thus avoiding absorption or trapping along the wall. The valve F is finally set to hold the radon in place.

In addition to the α-ray reaction sphere D, a separate cylinder I for the photo reaction is placed in the same circulation system but in a separate thermostat G. Two photo reaction chambers may also be separately placed in thermostats at different temperatures, which provides a most accurate means of determining temperature coefficient, since difference in sensitivity is eliminated. The hydrogen chloride formed in D and I may be continuously removed by circulating the gases through the water trap H of low head.

Calibration of Instruments.—The graduated capillaries used to measure the velocity of reaction were calibrated by sealing to the apparatus a slender gas buret of known volume so as to determine the movement of the capillary index corresponding to the removal from the capillary of definitely known amounts of gas.

The quantities of radon used were determined by γ-ray comparison with standard radium tubes. This measurement was most conveniently and accurately made while the radon was still sealed (four hours or longer after collection) in the small glass tube later broken inside the apparatus. The method of handling after breaking insures that all the radon reaches the α-ray bulb. This is verified by absence of luminous spots (after four hours) along the tube through which the radon has passed.

The light source was a 75-watt, nitrogen-filled tungsten lamp. The following procedure was employed to determine the energy absorption from this lamp by the reaction mixture under certain definite conditions. A radiation standard lamp was obtained from the Bureau of Standards, the total radiation from which at two meters' distance in a definite direction was known in absolute units for various currents. The radiation was allowed to fall on a ten-element, bismuth-silver thermopile connected to a sensitive d'Arsonval galvanometer. The resistance of the pile was about 10 ohms, that of the galvanometer about 15 ohms. The galvanometer had

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[18] Ref. 3, p. 76.

[19] Bardwell and Doerner, This Journal, **45**, 2593 (1923).

[20] Ref. 3, pp. 77–78.

a sensitivity of about 5mm. deflection per millivolt when the total resistance of the circuit was 40 ohms, the critical damping resistance. With 25 ohms it became stationary after two or three short swings. The deflections were read on a ground-glass scale at about 1 meter distance. The galvanometer, although not the most sensitive type, was free from zero creep and gave almost instantaneous readings and deflections of about the right order for use with the radiation standard.

Chlorine absorbs such a small portion of white light that the actual absorption is not easily measurable by the difference in total radiation transmitted to the pile through the reaction cell with and without chlorine present. A filter of about 5 cm. of 10% cupric sulfate solution was used to limit the spectral region. A 400-watt, nitrogen-filled tungsten lamp was used behind the filter to give a large deflection. Between the filter and the thermopile was placed a cylindrical cell about 15 cm. long with plane ends to prevent reflection. This was filled to $^1/_2$ atmosphere of chlorine which by means of a side tube and liquid air could be removed at will. Readings were made with and without chlorine. It was found that 23% of the light passing the filter was absorbed by chlorine and that the actual percentage could be determined fairly accurately.

This cell was then sealed into the circulating system in place of the α-ray reaction bulb, and the same lamp under the same current with the same filter was placed at the same distance from an aperture in front of one of the windows that it had formerly been from the thermopile in the first part of the calibration described above. The absolute amount of energy reaching the aperture and the amount of energy that would be absorbed by the chlorine in the H_2-Cl_2 mixture could be readily calculated. The absorption of hydrogen in the visible region is so low that it could be neglected. The rate of reaction under the influence of this light under these conditions was directly compared for mixtures of various sensitivities with that under the influence of the standard 75-watt lamp illuminating the light reaction bulb used throughout the experiments. (See Tables I, II and III.)

Methods of Calculation.—The number of molecules reacting per unit time was calculated by first transforming the rate of the displacement of the thread into cubic centimeters per minute by means of the calibration of the thread. This volume was then calculated to 0° and one atmosphere by means of the ordinary gas laws. From considerations of the density of pure chlorine and pure hydrogen, the number of molecules in 1 cc. of the mixture was taken to be 2.71×10^{19}. From this value the number of molecules reacting per minute was calculated.

Calculation of the Number of Ions Formed.—To estimate the number of ions formed in the reaction vessel the methods that have been standardized by Lind were used. The amount of radon in the apparatus at any time was calculated using the decay constant of radon from the lapse of time since the measurement of the amount of radon against the standard radium tube. The number of alpha particles emitted per second by each millicurie of emanation in equilibrium with its active deposit was taken to be 1.116×10^8. From this, there must be subtracted a correction for those which are intercepted by the neck and tip of the α-ray bulb. The α-ray bulb used had a diameter of 1.59 mm. The diameter of the tip was 0.390 mm. and the diameter of the neck was 0.85. A total correction of 10.1% should therefore be subtracted. The effective number of alpha particles per millicurie for this bulb was, therefore, 1.003×10^8 per second. The radius of the α-ray reaction bulb was 2.55 cm.

Correcting for the size of the α-ray bulb itself, the path of each alpha particle was 2.47 cm. A study of the characteristics of an α-ray bulb as a source of ionization (Part IV)[19] indicates that the average intensity of ionization is very nearly constant for distances of 2–3 cm. and the value for air is 2.8×10^4 ions per alpha particle per centimeter of path. The ionization in a mixture of chlorine and hydrogen has not been directly determined, but it may be readily calculated since the stopping power is a property that is approximately additive for the atoms that make up a substance.

Taking the specific ionization of hydrogen as 0.24 (relative to air) and that of chlorine as 2.42, a mixture of equal volumes would correspond to 1.33 or to 3.72×10^4 ion pairs from one alpha particle per centimeter of path. Therefore, in a path of 2.47 cm. each alpha particle would produce 8.45×10^4 ion pairs at 0° or 7.74×10^4 at 25°. For the α-ray bulb and reaction sphere used, the value for all calculations of ionization is, therefore, 7.84×10^4 ion pairs per second per millicurie of radon.

Calculations of Quanta Absorbed.—In the calculations on the standardization of the lamp the data in Table I were used.

TABLE I

CALIBRATION OF THERMOPILE AGAINST RADIATION STANDARD B. AND S. NO. C-50

Amperes through filament	Radiation intensity per sq. mm., watts	Av. deflection	Watts per sq. mm. per mm. deflection
0.350	85.2×10^{-8}[a]	26.5	3.22×10^{-8}
.400	112.6×10^{-8}[a]	35.2	3.20×10^{-8}
			Av. 3.21×10^{-8}

[a] Calibration of the Bureau of Standards for the intensity of radiation at points 2 meters distant from lamp.

The deflections given are the average of a large number of observations. The correction for the straight scale is negligible for these small angles. The data show that the intensity of radiation may be taken to be proportional to the deflection read. With the 400-watt lamp and copper sulfate screen in position before the thermopile a large number of alternate observations were taken of which Table II shows the average.

The same lamp and filter were then placed in position before the aperture beyond which the light passed through the cell now sealed into the

TABLE II

CALIBRATION OF MONOCHROMATIC LIGHT AGAINST THERMOPILE

	Deflection of galv.	Watts per sq. mm.	Absorption, %
Cl_2 in cell	66.5	2.17×10^{-6}	23.4
Cl_2 frozen out	86.7	2.78×10^{-6}	

apparatus and filled with a mixture of hydrogen and chlorine. The area of the aperture was 22.5 sq. mm. The rate at which energy passed through the aperture was therefore 62.6×10^{-6} watt. The rate of energy absorption by the chlorine was 14.8×10^{-6} watt or 148 ergs per second.

Since the light after leaving the aperture suffered the same number of reflections in going through the glass wall of the thermostat and one end of the cell that it did in going through the two ends of the cell in the measurements above, the loss by reflection was practically compensated.

From considerations of the absorption curves of chlorine, copper sulfate solutions and glass and from the distribution of energy in light from a tungsten filament at 2700 °K., the wave length of 4100 Å. was arrived at as the probable average value of wave length absorbed by the chlorine in the cell used here. Graphical methods were used and it is believed that the value taken cannot be more than 5 or 10% in error. A quantum of this wave length contains 4.79×10^{-12} erg. Dividing this into the ergs absorbed per second gives 3.09×10^{13} quanta absorbed per second. The rate of reaction under the influence of this light was then compared with the rate obtained with the 75-watt white light which was used as a convenient intermediate standard throughout the experiments. Assuming that the number of molecules reacting is proportional to the quanta absorbed in the same sensitivity of mixture, the number of quanta absorbed from the white light could be calculated. The data taken in this comparison are shown in Table III.

TABLE III

COMPARISON FOR MONOCHROMATIC AND WHITE LIGHT AT DIFFERENT SENSITIVITIES

400-Watt light with filter[a]	75-Watt lamp (white light)	
Cc. reacting per minute	Cc. reacting per min.	Quanta absorbed per sec. $\times 10^{-13}$
0.11	0.073	2.05
.32	.23	2.22
.96	.68	2.19
1.06	.74	2.16
2.55	1.73	2.09
2.53	1.75	2.14
5.70	3.98	2.16
6.04	4.24	2.17

[a] 3.09×10^{13} quanta were absorbed per second. Av. quanta absorbed per sec., 2.15×10^{13}.

Preliminary Work.—One of the first objects was to find out whether change of sensitivity toward light would be the same as toward alpha radiation, and whether the two effects would be additive for a given sensitivity.

After some use of light in testing and perfecting the apparatus, 13 millicuries of radon was introduced into the α-ray bulb. This quantity was adjudged a suitable one on the basis of Taylor's results, but the reaction was so rapid that it could not be measured with any accuracy and the electrolytic generator had to be operated continuously to maintain the gas supply. Evidently Taylor's mixture was relatively insensitive. It was found necessary to admit some air (oxygen) and wait eight days for the decay of radon before quantitative work could be begun.

Parallelism and Additivity of the Effects of Photo- and of Alpha Radiation.—Starting with a rather insensitive mixture obtained by allowing a small portion of air initially to remain in the apparatus, a series of experiments at different sensitivities was made. *It could thus be easily established that sensitivity rises and falls proportionately for photo- and alpha radiation, and that the two effects when superimposed are strictly additive.*

Creep in Sensitivity.—The sensitivity of the mixture seldom remained constant for any length of time but was usually observed to creep up or down more or less rapidly. For this reason alternate exposures were always made. For slow reactions the water thread was allowed to move about one-third the length of the graduated capillary under the influence of one radiation, say with alpha particles alone, then the light would be switched on and readings taken until the thread was about two-thirds across; then another series would be taken again with only alpha particles acting. The middle series was then compared against the average of the two series on each side. Where the change in sensitivity is uniform this should give correct results. For rapid rates it was necessary to take in fresh gas from the generator between readings. The change in sensitivity was, however, not much greater, if any, than when gas was not introduced. Explanations for this creep in sensitivity are so far not entirely satisfactory. In one or two cases an abrupt change in sensitivity was traced to moisture collecting on the tube above the α-ray reaction chamber and running down into the chamber where it was acted on by alpha particles, liberating oxygen. However, even in work where no radon was present the same gradual creep was observed. Just why inhibitors should be produced in one case and destroyed in another with conditions apparently the same is difficult to understand. The fact is important, however, for it seems that only comparisons that are nearly simultaneous can be relied on. An accurate study of the kinetics of this reaction by varying the concentration of the constituents and other factors does not seem possible, at least not with the methods so far employed. This fact probably accounts for the many discrepancies between the results of different investigators reported in the literature.

Comparison of the Photo- and α-Ray Rate of Reaction.—Table IV contains the experimental data and results of calculation. Col. 1 shows the date and hour, Col. 2 the quantity of radon in millicuries, Col. 3 the calculated total ionization produced per second by the alpha radiation of radon, RaA and RaC, Col. 4 the rate of reaction due to α-rays in terms of displacement in the index capillary in divisions per minute, Col. 5 the molecules of hydrogen chloride formed per second as calculated from 4. Col. 6 (5 divided by 3) shows the number of molecules of hydrogen chloride synthesized per ion pair at different sensitivities. Col. 7 gives the number of light quanta per second absorbed by chlorine, Col. 8 the rate of reaction due to light in divisions per minute, Col. 9 the molecules of hydrogen chloride synthesized per second by light. Col. 10 (9 divided by 7) gives the number of molecules of hydrogen chloride synthesized per light quantum at different sensitivities. Col. 11 shows the percentage change in sensitivity of the mixture between the first and last intervals, Col. 12 shows the character of the intervals (*a* indicating periods of alpha radiation and *l* periods of *light* plus alpha radiation). Of course, in the data reported for light in Cols. 7, 8 and 9, the α-ray effect has been subtracted, having been shown to be strictly additive. Finally, Col. 13 shows the constant ratio of the synthesis per ion pair to that per light quantum for all sensitivities varying over a 500-fold range. The significance of the absolute value found will be discussed later.

Inspection of Col. 11 shows that the change of sensitivity during a single series was sometimes small, sometimes greater, and in either direction. It is evident that a fairly large percentage change does not affect the ratio $(M/N):(M/q)$, provided the change be uniformly distributed. In other words, uniformity of change insures that the mean of the sensitivity in the first and third periods is equal to that of the second. Accordingly, the values used are the means of corresponding periods. The uniformity of change was controlled by frequent readings (not given) within the whole periods of one to ten minutes, depending on sensitivity. In the case of sudden deviation or other known causes of error, the data were discarded. We exclude arbitrarily from the mean those values where sensitivity changed by as much as 20%, although it will be seen that some of those showing as high as 30% deviation of sensitivity agree with the mean ratio, while greater deviation from the mean is shown by some of low change of sensitivity. The mean is but little affected by such exclusion, which was made merely to have some definite principle of selection.

Temperature Coefficient.—During the period of experimentation before the light reaction bulb was placed in a separate thermostat in the circulating system, an attempt was made to determine the temperature coefficient. The reaction rate at 25° was determined, then the system was cooled to 10°. A decrease of about one-half was observed in both the reaction rates under the influence of light and under the influence of alpha particles. On raising the temperature to 35°, however, the rates had still

TABLE IV

A COMPARISON OF THE CHEMICAL EFFECTS OF LIGHT AND OF ALPHA PARTICLES

Reaction: $H_2 + Cl_2 = 2HCl$. N = number of ion pairs; q = number of quanta; M = number of molecules of hydrogen chloride

1 Date, 1926	Hour	2 Radon, mc.	3 Ion pairs per second × 10^{-13}	4 Div. per min., α-rays	5 Molecules per sec. × 10^{-17}	6 $\frac{M_{HCl}}{N_{ion\ pairs}}$	7 Quanta per sec. × 10^{-13}	8 Div. per min., light	9 Molecules per sec. × 10^{-17}	10 M/q	11 Change in sensitivity, %	12 Intervals	13 $\frac{M/N}{M/q}$
1/11	4.00 P.M.	1.85	1.43	8.5	0.130	910	5.10	8.1	0.124	243	− 2.6	*lalal*	3.68
1/11	6.00	1.82	1.41	10.2	.157	1112	5.10	9.4	.145	285	+ 6.0	*lal*	3.90
1/11	7.00	1.80	1.40	75	1.15	8300	5.10	81.2	1.25	2450	−31.0	*lal*	(3.38)
1/13	12.05	1.34	1.04	65	0.995	9540	5.10	87.6	1.35	2650	+ 1.0	*lal*	3.60
1/13	1.00	1.34	1.04	110	1.68	16160	5.10	143	2.19	4300	−10.0	*ala*	3.76
1/13	1.30	1.33	1.03	140	2.14	20600	5.10	185	2.84	5570	− 5.0	*lal*	3.70
1/13	2.00	1.32	1.02	39	0.598	5840	5.10	53.6	0.82	1610	− 7.0	*lal*	3.62
1/13	2.40	1.32	1.02	60	.918	9000	5.10	78.6	1.21	2380	− 4.0	*lal*	3.78
1/13	3.10	1.31	1.02	96	1.47	14480	5.10	129	1.98	3890	+25	*lal*	(3.72)
1/13	3.45	1.30	1.00	110	1.68	16820	5.10	147	2.26	4430	+ 2.0	*lal*	3.80
1/13	4.35	1.29	1.00	103	1.58	15800	5.10	144	2.20	4320	− 4.0	*lal*	3.66
1/13	6.00	1.26	0.98	54	0.826	7840	5.10	72	1.11	2180	− 2.0	*ala*	3.60
1/14	10.30 A.M.	1.08	.84	23	.354	4240	5.10	87	0.57	1120	+33	*lal*	(3.78)
1/14	11.20	1.07	.83	13	.199	2400	5.10	21	.326	640	− 6	*alal*	3.76
1/14	12.05 P.M.	1.07	.83	26	.398	4800	5.10	40.5	.62	1230	+28	*alal*	(3.90)
1/14	2.10	1.05	.82	51	.780	9580	5.10	88	1.35	22650	−15	*lal*	3.62
1/14	5.15	1.03	.80	17.5	.268	3340	5.10	30	0.46	910	−14	*lal*	3.66
1/19	12.30	0.452	.35	9.1	.138	3940	2.15	14.9	.228	1060	− 1	*lal*	3.72
1/19	2.10	.445	.345	112	1.71	49000	2.15^a	188	2.88	13400	−17.5	*la la*	3.66
1/19	6.30	.431	.334	141	2.14	64200	1.37^a	157	2.41	17600	+ 1.3	*lal*	3.64
1/20	9.40 A.M.	.382	.296	122	1.87	63200	2.15	240	3.67	17100	+ 7.5	*lal*	3.70
1/20	1.00 P.M.	.373	.289	260	3.98	137800	1.37^a	329	5.04	36800	+13	*lal*	3.74
1/21	6.00	.299	.224	710	10.7	512000	2.15	1960	29.9	139000	..	*la*	3.68
													Av. 3.72

[a] Alpha particles and light absorbed in the same reaction chamber.

further decreased showing that not a temperature coefficient but a decrease in sensitivity had been observed.

This method was obviously so unsatisfactory that the light bulb was placed in a separate thermostat in the circulation system. Observations were made with the reaction bulbs at 25° and then the temperature of the light reaction bulb was raised to 100°. The rate of reaction was found to have increased considerably for the light reaction, apparently confirming the results of Bevan[21] and of Padoa and Butironi.[22] However, when the α-ray reaction bulb, *which had remained at 25°*, was illuminated, it too showed a corresponding increase in rate of reaction, showing that merely the *sensitivity* had been changed by heating and that the *true temperature coefficient* over this range was so small as to be hardly noticeable.

To obtain more accurate data on the temperature coefficient, the α-ray reaction bulb was replaced by a plain light reaction bulb. A series of experiments was run at different sensitivities with the one bulb at 25° and the other at 100°. The results are given in Table V.

TABLE V

DATA FOR DETERMINING THE TEMPERATURE COEFFICIENT OF THE PHOTO REACTION

Reaction bulb at 100°			Reaction bulb at 25°			
Quanta per sec. $\times 10^{-13}$	Molecules per sec. $\times 10^{-17}$	M/q $\times 10^{-3}$	Quanta per sec. $\times 10^{-13}$	Molecules per sec. $\times 10^{-17}$	M/q $\times 10^{-3}$	Temp. coeff.
2.15	2.03	9.44	3.09	2.8	9.05	1.006
2.15	1.99	9.26	3.09	2.67	8.63	1.009
2.15	1.94	9.02	3.09	2.75	8.9	1.002
2.15	39.3	183	3.09	28.3	91.5	1.097
2.15	35.9	167	3.09	24.7	79.9	1.103
2.15	32.6	152	3.09	23.2	75.0	1.099
2.15	1.12	5.2	1.37	0.74	5.4	0.992

The number of quanta absorbed at 100° is taken as the same as that found in the calibration at 25°. There is a slight error made in this due to rarefaction of the gas, but it is probably quite small. Consulting the data of v. Halban and Siedentopf[23] for the absorption of light by chlorine we find that wave lengths of light lying in the region of the strong absorption band are more than 90% absorbed by a length of chlorine at 0.5 atmosphere equal to the length of the reaction vessel and small changes in the density would not affect the total amount absorbed. The light through the filter was, of course, not entirely monochromatic. The wave lengths lying in the band would be almost entirely absorbed, while those lying over in this region of higher wave lengths are only feebly absorbed. The slight change in density due to raising the reaction vessel to 100° would not affect the absorption of these. The absorption of only a very small part of the ra-

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[21] Bevan, *Proc. Cambridge Phil. Soc.*, **12**, 398 (1904).

[22] Padoa and Butironi, *Gazz. chim. ital.*, [II] **47**, 6 (1917).

[23] v. Halban and Siedentopf, *Z. physik. Chem.*, **103**, 80 (1923).

diant energy lying in the region of moderate absorption would be affected and this amount would be negligible.

The values in Cols. 2 to 6 need no further explanation. The temperature coefficient in Col. 7 is calculated on the usual 10° basis from the formula $\log K = [10°/(100-25°)][\log(R_{100}/R_{25})]$, where K is the temperature coefficient and R_{100} and R_{25} are the respective rates of reaction at 100° and 25°.

Upper Limit of Sensitivity.—Since heating the gases to 100° usually increased the sensitivity it was thought that this was due to the destruction of an inhibitor. To determine whether oxygen was removed, a mixture known to contain air was heated to 100°. The sensitivity increased only three-fold and then became nearly constant. Further heating failed to increase the sensitivity, from which it was concluded that at least one other inhibitor more powerful but less stable than oxygen was originally present but had been destroyed by heating. Chlorine monoxide suggests itself as the only compound probably present which is unstable and does not produce an induction period. That it might be formed by a slight reaction of the chlorine with water was indicated by the following incident. On January 23rd, when the radon had decayed to 0.22 millicurie, the gases in the light and α-ray reaction chambers had reached a high sensitivity. The light reaction bulb had been standing at 100° for about one-half hour without circulation. On starting the pump this mixture was drawn over into the α-ray reaction bulb and apparently had exceedingly high sensitivity, for the small amount of radon left was sufficient to explode the mixture. This indicated that a small amount of an inhibitor is continually produced by the circulation of the gases through the water and that this was destroyed by heat. Although a sensitivity of 512,000 molecules per ion-pair was the highest measured, the above incident would suggest that this is not the upper limit possible of attainment.

Discussion.—The foregoing experiments demonstrate that the combination of hydrogen and chlorine induced either by light or by alpha radiation is a chain reaction. The fact that variation of sensitivity (by changing the amount of inhibitor) produces exactly the same change in rate of both reactions must mean that the reaction chains in both cases are of equal length, and hence the mechanisms of the secondary reactions are identical whatever they may be.

The nearly four-fold excess of the value of M/N over M/q for any sensitivity is reduced to less than two-fold, by taking account of the negative ions (as well as the positive) formed by free electrons attaching themselves to chlorine molecules. To explain the remaining difference we must assume that either the chains in the case of ionization are twice as long or that there are twice as many of them. The first assumption would be difficult to reconcile with the constancy of $(M/N)/(M/q)$ for all sensitivities; hence, we are left but to explain why an *ionized* chlorine molecule either positive or negative sets up twice as many chains at 25° as an *excited* one. Is the ion intrinsically twice as effective as the excited molecule? The result of light reaction at 100° indicates that it is not, but rather that the molecules excited by quanta are only about 50% efficient at 25° and approach or reach 100% at 100°. This interpretation is based on a comparison assuming that the α-ray reaction is 100% efficient and is without temperature coefficient between 25° and 100°. This latter was not tested experimentally for this reaction, but has been found true between +25° and —75° for the combination of hydrogen and oxygen,[24] and from what we know of ionization by collision at moderate temperatures seems to have general probability.

The experiments seem definitely to prove that in whatever way the reaction chain be initiated, it has the same length in a mixture of the same sensitivity. This confirms Christiansen's[25] idea that the length of the chain determines the speed of reaction. It must mean identical chain mechanism for photo- and for alpha radiation, but it does not tell us directly what that mechanism is. If we assume that the general evidence of atomic-chain mechanism, such as Bodenstein[26] has recently adduced for the hydrogen-bromine reaction, points toward the Nernst[7] mechanism for hydrogen-chlorine, then the following mechanisms might be proposed.

For light:

$$Cl_2 + 1h\nu = Cl_2'$$
$$Cl_2' + Cl_2 = Cl_2 + 2Cl \text{ (50\% efficient at 25°; 100\% efficient at 100°)}$$

For alpha radiation:

$$Cl_2 + (\alpha) = Cl_2^+ + (-);\ Cl_2 + \ominus = Cl_2^-$$
$$Cl_2^+ + Cl_2^- = 4Cl \text{ (100\% efficient at 25° and at 100°)}$$

Since the ionized state is a more energetic one than the excited state of a molecule, the greater number of atoms resulting from an ion pair is plausible from the energetic standpoint; but comparing with other ionization reactions the mechanism formulated for alpha radiation receives no support. That Cl_2^+ and Cl_2^- ions, both very low in concentration, should collide without first having clustered with hydrogen molecules is not probable. Of course, we may assume: $Cl_2^+ \longrightarrow Cl^+ + Cl$ and $Cl_2^- \longrightarrow Cl^- + Cl$, to initiate four chains, but it seems more plausible to assume

$$\begin{array}{c} Cl_2^+ + H_2 = Cl_2H_2^+ \\ Cl_2^- + H_2 = Cl_2H_2^- \\ \hline Cl_2H_2^+ + Cl_2H_2^- = 2H_2Cl'_2 \end{array}$$

$2H_2Cl_2' + 2Cl_2 = 4HCl + 4Cl$, again arriving at the Nernst chain.

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[24] Lind and Bardwell, THIS JOURNAL, **46**, 2006 (1924).

[25] Christiansen, *J. Phys. Chem.*, **28**, 145 (1924).

[26] Bodenstein and Lütkemeyer, *Z. physik. Chem.*, **114**, 208 (1924). Bodenstein and Jung, *ibid.*, **121**, 127 (1926).

Either primary reaction ionization or excitation could be equally well directed either into the "hot molecule" or into the Nernst chain, so that the present experiments give no decision.

One might incline to interpret the results as indicating that the primary steps as well as the secondary ones are identical for the photo- and α-ray reactions. Since we cannot assume ionization for the photo reaction, it would necessitate assuming excitation for the α-ray reaction. There is no direct evidence on this point. If the electron returned alone it might well pass into a higher orbit, but this could hardly occur before its capture by a chlorine molecule, making the mechanism proposed above the more probable for the primary step, rather than excitation.

No further discussion of the temperature coefficient appears necessary than to say that the present data are not regarded as complete enough to justify the inquiry as to whether the energy increment added to the light quantum would make up the necessary heat of dissociation of chlorine. This will be reserved for future work when it is hoped to be able to follow the transition in quantum efficiency over the range of 25° to 100° and to determine experimentally whether the α-ray synthesis has a temperature coefficient.

Support of the Einstein Photochemical Equivalence Law.—The results of the present experiments appear not only to support the Einstein equivalence law but to bring evidence of a new and perhaps more definite character. Previous efforts to test this law have been concerned with establishing equality between the number of quanta absorbed and the number of molecules brought to reaction. While some isolated cases of equivalence have been found, they are exceptional. Usually the yield of the primary reaction is completely obscured by a much larger quantity of a secondary reaction whose relation to the primary is speculative or unknown. Although it has been frequently reiterated that failure of the secondary yield to correspond molecule for quantum with the light absorbed does not invalidate the law, there were no means of obtaining direct evidence regarding the obscured primary quantum effect.

Here, however, we have two entirely distinct physical agents, light and alpha particles, acting through different primary steps, excitation and ionization, producing total reaction greatly in excess of the unit quantities involved in the primary steps, and yet the total quantities of action referred back to the unit, in each case, are equal to each other. Hence, we must conclude that each unit has distinct reality, and since both are determined by quite different methods, we must admit that the ionic relationship lends independent weight to the quantic one forming the basis of the photochemical equivalence law. Hence, the validity of the Einstein law is indirectly demonstrated for the primary reaction, even when it is greatly exceeded by the secondary yield.

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Summary

1. The rates of synthesis of hydrogen chloride by light and by alpha radiation were determined using a modified Bunsen and Roscoe actinometer, in which the hydrogen-chlorine mixture is circulated by means of an all-glass magnetic pump through three chambers: (a) for light reaction, (b) for α-ray reaction and (c) for hydrogen chloride absorption in water.

2. In the same mixture, the number of hydrogen chloride molecules formed at 25° per ion pair (M_{HCl}/N) exceeds the number per quantum (M_{HCl}/q) by nearly 4-fold, instead of being 250-fold smaller. The ratio at 25° of N/q remains constant for all sensitivities through a range of 500-fold.

3. By considering total ions of both signs instead of ion pairs, the difference between ion and quantum efficiency at 25° is reduced to two-fold, and at 100° it disappears altogether, one quantum absorbed and one ion producing equal reaction for the same sensitivity of gases.

4. New and independent support of the Einstein photochemical equivalence law is seen in the evidence just stated.

5. At least two inhibitors seem to be present, oxygen and possibly Cl_2O. The latter, the more powerful, is probably formed by the action of chlorine on water.

6. The highest photo yield, $M/q = 139{,}000$ (corresponding to $M/N = 512{,}000$), is not believed to represent the maximum sensitivity, since a mixture was obtained by heating in the absence of circulation that was exploded by only 0.22 millicurie of radon.

7. The apparently high temperature coefficients are due to the effect of temperature in enhancing the sensitivity, not to a true temperature coefficient. The coefficients probably consist of two opposite factors; one, a true temperature coefficient, is the energy increment, imparted kinetically to the product already activated by light absorption, thus increasing the fraction of activated molecules actually reacting as the temperature becomes higher, until at 100° it apparently reaches unity; the other effect, oppositely directed, consists in the retarding influence of the inhibitor as enhanced by higher temperature.

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